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(54) PRODUCTION OF PLATINUM ALLOY CATALYST FOR PHOSPHORIC ACID TYPE FUEL CELL**(57)Abstract:**

PURPOSE: To improve elution resistance and activity when used as the phosphoric acid type fuel cell by depositing and alloying base metal on the platinum or platinum alloy particles contained in the catalyst, lessening independent particles of the platinum and the base metal and making distribution of alloy component ratio more narrowly.

CONSTITUTION: The catalyst deposited platinum or platinum alloy on carbon powder is soaked in hot water and dispersed by an ultrasonic homogenizer under stirring, then one or two kinds among chromium, manganese, cobalt, nickel, copper are plated on the dispersed catalyst by electroless plating, and alloyed with the platinum or platinum alloy particles, thus the objective platinum alloy catalyst for the phosphoric acid type fuel cell is obtained.

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PRODUCTION OF PLATINUM ALLOY CATALYST FOR PHOSPHORIC ACID TYPE FUEL CELL

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Abstract

PURPOSE: To improve elution resistance and activity when used as the phosphoric acid type fuel cell by depositing and alloying base metal on the platinum or platinum alloy particles contained in the catalyst, lessening independent particles of the platinum and the base metal and making distribution of alloy component ratio more narrowly.

CONSTITUTION: The catalyst deposited platinum or platinum alloy on carbon powder is soaked in hot water and dispersed by an ultrasonic homogenizer under stirring, then one or two kinds among chromium, manganese, cobalt, nickel, copper are plated on the dispersed catalyst by electroless plating, and alloyed with the platinum or platinum alloy particles, thus the objective platinum alloy catalyst for the phosphoric acid type fuel cell is obtained.

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(57)【要約】

(57)[SUMMARY]

【目的】

触媒中の白金又は白金合金の粒子上に卑金属を担持し合金化して、白金単独粒子や卑金属単独粒子を少なくし、且つ合金組成比の偏りをより小さくして、りん酸型燃料電池に用いた際の耐溶出性及び活性を向上させることのできるりん酸型燃料電池用白金合金触媒を作ることのできる方法を提供する。

[OBJECT]

Base metal is supported and alloyed on the particle of the platinum or the platinum alloy in the catalyst.

A platinum independent particle and a base metal independent particle are decreased, and deviation of an alloy composition ratio is made smaller. The method of making the phosphoric acid type fuel battery platinum alloy catalyst which can improve the dissolubility-resistant and the activity at the time of using for a phosphoric acid type fuel cell is provided.

【構成】

白金又は白金合金をカーボン粉末に担持した触媒を温水に浸し攪拌しながら超音波ホモジナイザーで分散し、然る後この分散

[SUMMARY OF THE INVENTION]

An ultrasonic homogenizer disperses, soaking a catalyst which supported platinum or the platinum alloy with the carbon powder in warm water, and stirring it.

After that, the electroless plating of 1 kind or the

した触媒に、クロム、マンガ、鉄、コバルト、ニッケル、銅の1種又は2種を無電解めっきし、触媒中の白金又は白金合金粒子と合金化することを特徴とするりん酸型燃料電池用白金合金触媒の製造方法。

【特許請求の範囲】**【請求項1】**

白金又は白金合金をカーボン粉末に担持した触媒を温水に浸し攪拌しながら超音波ホモジナイザーで分散し、然る後この分散した触媒に、クロム、マンガ、鉄、コバルト、ニッケル、銅の1種又は2種を無電解めっきし、触媒中の白金又は白金合金粒子と合金化することを特徴とするりん酸型燃料電池用白金合金触媒の製造方法。

【発明の詳細な説明】**【0001】****【産業上の利用分野】**

本発明は、りん酸型燃料電池用白金合金触媒の製造方法に関する。

【0002】**【従来の技術】**

従来、りん酸型燃料電池用白金合金触媒を製造するには、白金をカーボン粉末に担持した触媒

2 kinds of chromium, manganese, iron, cobalt, nickel, and copper is carried out to this dispersed catalyst.

It alloys with the platinum or the platinum alloy particle in the catalyst.

A manufacturing method of a phosphoric acid type fuel battery platinum alloy catalyst characterized by the above-mentioned.

【CLAIMS】**【CLAIM 1】**

An ultrasonic homogenizer disperses, soaking a catalyst which supported platinum or the platinum alloy with the carbon powder in warm water, and stirring it.

After that, the electroless plating of 1 kind or the 2 kinds of chromium, manganese, iron, cobalt, nickel, and copper is carried out to this dispersed catalyst.

It alloys with the platinum or platinum alloy particle in the catalyst.

A manufacturing method of a phosphoric acid type fuel battery platinum alloy catalyst characterized by the above-mentioned.

【DETAILED DESCRIPTION OF INVENTION】**【0001】****【INDUSTRIAL APPLICATION】**

This invention relates to the manufacturing method of a phosphoric acid type fuel battery platinum alloy catalyst.

【0002】**【PRIOR ART】**

Conventionally, in order to produce a phosphoric acid type fuel battery platinum alloy catalyst, a catalyst which supported platinum with the carbon powder is soaked in water.

を水に濡らし、これに合金成分となる1種又は2種の卑金属を含む溶液、即ちクロム、マンガ、鉄などは硝酸塩溶液、コバルト、ニッケル、銅などはアンモニア性アルカリ性溶液として加えて混合し、1時間程度攪拌してスラリー状にした後、乾固させた。その後水素気流下で900℃前後に加熱して、還元、合金化処理を行っていた。この従来の製造方法で製造できる白金合金触媒は、合金組成比がモル比で $Pt : \text{卑金属} = 1 : 1$ が目標であるにもかかわらず、卑金属を含む溶液の混合量を増やしても、また長時間攪拌しても $1 : 0.3$ 程度までしか合金化されない。また白金を担持させたカーボン粉末の触媒を溶液と混合させた後乾固させる為、卑金属成分が塩の結晶となって不均一に析出し、触媒中で卑金属成分の偏在が起こる。これを水素中で合金化処理を行っても卑金属と合金となった白金合金のほか白金単独或いは卑金属単独の粒子もでき、特に卑金属単独の粒子は酸で容易に洗い流されてしまう。

【0003】

【発明が解決しようとする課題】

そこで本発明は、触媒中の白金又は白金合金の粒子上に卑金属を担持し合金化して、白金単独粒子や卑金属単独粒子を少なくし、且つ合金組成比を現状の $1 : 0.3$ から $1 : 1$ に近づけて

To this the solution which contains 1 kind or 2 kinds of base metal forming an alloy content, that is, chromium, manganese, iron, etc. are added as a nitrate solution. Cobalt, nickel, copper, etc. are added as an ammonia property alkaline solution. The dryness was carried out, after mixing, and carrying out an about one hour stir and making the form of a slurry.

After that, it heated before and after 900 degree C under the hydrogen air current, and reduction and the alloying process were performed.

The platinum alloy catalyst which can be produced by this conventional manufacturing method, Although an alloy composition ratio target is molar ratio $Pt : \text{base metal} = 1 : 1$. Even if it increases the amount of mixing of the solution containing base metal or it stirs for a long time, it is alloyed only to about $1 : 0.3$.

Moreover after mixing a catalyst of carbon powder which made platinum support with a solution, in order to carry out a dryness, a base metal component makes the crystal of a salt, and precipitates non-uniformly, and the maldistribution of a base metal component occurs in a catalyst.

Even when it performs this in hydrogen an alloying process, A particle platinum independent or base metal independent besides the platinum alloy which became base metal and the alloy is also made.

In particular a base metal independent particle will be easily flushed from an acid.

【0003】

【PROBLEM ADDRESSED】

Then this invention, Support and alloy base metal on the particle of the platinum or the platinum alloy in the catalyst, and a platinum independent particle and a base metal independent particle are decreased. And an alloy composition ratio is brought close to $1 : 1$ from present $1 : 0.3$, and deviation of the alloy composition ratio between the alloy

触媒中の合金微粒子間の合金組成比の偏りをより小さくして耐溶出性及び活性を向上させることのできるりん酸燃料電池用白金合金触媒の製造方法を提供しようとするものである。

microparticles in the catalyst is made smaller. It is going to provide the manufacturing method of the phosphoric acid fuel battery platinum alloy catalyst which can improve dissolubility-resistant and an activity.

【0004】

【0004】

【課題を解決するための手段】

上記課題を解決するための本発明のりん酸燃料電池用白金合金触媒の製造方法は、白金又は白金合金をカーボン粉末に担持した触媒を温水中に浸し攪拌しながら超音波ホモジナイザーで分散し、然る後この分散した触媒に、クロム、マンガン、鉄、コバルト、ニッケル、銅の1種又は2種を無電解めっきし、触媒中の白金又は白金合金粒子と合金化することを特徴とするものである。

【SOLUTION OF THE INVENTION】

The manufacturing method of the phosphoric acid type fuel battery platinum alloy catalyst of this invention for solving an above subject, An ultrasonic homogenizer disperses, soaking a catalyst which supported platinum or the platinum alloy with the carbon powder in warm water, and stirring it.

After that, the electroless plating of 1 kind or the 2 kinds of chromium, manganese, iron, cobalt, nickel, and copper is carried out to this dispersed catalyst.

It alloys with the platinum in the catalyst, or a platinum alloy particle.

The above-mentioned characterizes it.

【0005】

【0005】

【作用】

上記のように本発明のりん酸燃料電池用白金合金触媒の製造方法では、白金又は白金合金をカーボン粉末に担持した触媒を分散し、これにクロム、マンガン、鉄、コバルト、ニッケル、銅の1種又は2種を無電解めっきし、触媒中の白金又は白金合金粒子と合金化するので白金単独粒子や卑金属単独粒子が少なくなり、且つ合金組成比の偏りが著しく減少し、触媒の耐溶出性及び活性が向上する。

【EFFECT】

At the manufacturing method of the phosphoric acid type fuel battery platinum alloy catalyst of this invention, as mentioned above, A catalyst which supported platinum or the platinum alloy with the carbon powder is dispersed. The electroless plating of 1 kind or the 2 kinds of chromium, manganese, iron, cobalt, nickel, and copper is carried out to this. Since it alloys with the platinum or a platinum alloy particle in catalyst, a platinum independent particle and a base metal independent particle decrease.

And deviation of an alloy composition ratio reduces remarkably and the dissolubility-resistant and the activity of a catalyst improve.

[0006]

【実施例】

本発明のりん酸型燃料電池用白金合金触媒の製造方法の実施例を説明する。

[0006]

[Example]

The Example of the manufacturing method of the phosphoric acid type fuel battery platinum alloy catalyst of this invention is explained.

[0007]

(1) 白金を 2.85 g 含む白金-カーボン触媒 12.85 g を沸とう水 180ml に浸し、攪拌しながら超音波ホモジナイザーで分散させた。次に塩化ニッケル 1.94 g、塩化コバルト 1.93 g、錯化剤として酒石酸ナトリウム 29.58 g、還元剤として塩酸ヒドラジン 13.49 g を 320ml の水溶液とし、50% NaOH 溶液で pH を 12.8 に調整した溶液を、前記白金-カーボン触媒のスラリーに全量一度に投入し、攪拌しながら超音波ホモジナイザーで 2 分間分散させた。そして 1 時間程攪拌した後、これを濾過し、さらに洗浄液が中性になるまで水で数回洗浄した。最後に水素気流下で 900℃前後に加熱して触媒中の白金粒子とニッケル及びコバルトを合金化処理した。

[0007]

(1) Soak 12.85g of the platinum-carbon catalysts containing 2.85g of platinum in 180 ml of boiling waters. The ultrasonic homogenizer was made to disperse, stirring.

Next, 1.94g of nickel chloride, 1.93g of cobalt chloride, 29.58g of sodium tartrate as a complex agent, 13.49g of hydrazine hydrochlorides as reducer. Make an above be 320 ml aqueous solution.

The whole quantity of the solution which adjusted PH to 12.8 with NaOH solution 50% is thrown at once into the slurry of an above-mentioned platinum-carbon catalyst.

2 minutes was dispersed with the ultrasonic homogenizer, stirring.

And this is filtered after stirring a 1 hour. Furthermore several times washing was carried out with water until cleaning liquid became neutral.

Finally, it heated before and after 900 degree C under the hydrogen air current, and the alloying process of the platinum particle, nickel and cobalt in the catalyst was carried out.

[0008]

(2) 白金を 1.95 g 含む白金-カーボン触媒 8.8 g を沸とう水 120ml に浸し、攪拌しながら超音波ホモジナイザーで分散させた。次に硝酸ニッケル 1.45 g、硝酸鉄 2.05 g 錯化剤として酒石酸ナトリウム 18.42 g 還元剤として、塩酸ヒドラジン 31.24

[0008]

(2) Soak 8.8g of the platinum-carbon catalysts containing 1.95g of platinum in 120 ml of boiling waters. The ultrasonic homogenizer was made to disperse, stirring.

1.45g of next nickel nitrates, 2.05g of iron nitrate, 18.42g of sodium tartrate as a complex agent, As reducer, 31.24g of hydrazine hydrochlorides. Make an above be a 200 ml solution.

The whole quantity of the solution which

g を 200ml の溶液とし、50% NaOH 溶液で PH を 12.8 に調整した溶液を、前記白金-カーボン触媒のスラリーに全量一度に投入し、攪拌しながら超音波ホモジナイザーで 1 分間分散させた。そして 1 時間程攪拌した後、これを濾過し、さらに洗浄液が中性になるまで水で数回洗浄した。最後に水素気流下で 900℃前後に加熱して触媒中の白金粒子とニッケル及び鉄を合金化処理した。

[0009]

(3) 白金を 2.85g 含む白金-カーボン触媒 12.85g を沸とう水 180ml に浸し、攪拌しながら超音波ホモジナイザーで分散させた。次に硫酸銅 3.53g、錯化剤として酒石酸塩 7.59g、PH 調整剤として水酸化ナトリウム 5.06g、還元剤としてホルムアルデヒド (37%) 25.3ml を 240ml の溶液とし PH 12.8 に調整した。この溶液を前記白金-カーボン触媒のスラリーに全量一度に投入し、攪拌しながら超音波ホモジナイザーで 1 分間分散させた。そして 1 時間程攪拌した後、これを濾過し、さらに洗浄液が中性になるまで水で数回洗浄した。最後に水素気流下で 900℃前後に加熱して触媒中の白金粒子と銅を合金化処理した。

[0010]

上記のように製造した各実施例のりん酸型燃料電池用白金合金触媒は、白金単独粒子やニッケル、コバルト、鉄、銅などの卑

adjusted PH to 12.8 with NaOH solution 50% is thrown at once into the slurry of an above-mentioned platinum-carbon catalyst.

1 minute was dispersed with the ultrasonic homogenizer, stirring.

And this is filtered after stirring a 1 hour. Furthermore several times washing was carried out with water until cleaning liquid became neutral.

Finally, it heated before and after 900 degree C under the hydrogen air current, and the alloying process of the platinum particle, nickel and iron in the catalyst was carried out.

[0009]

(3) Soak 12.85g of the platinum-carbon catalysts containing 2.85g of platinum in 180 ml of boiling waters. The ultrasonic homogenizer was made to disperse, stirring.

Next, 3.53g copper sulfate, 7.59g of tartrate as a complex agent, 5.06g of sodium hydroxide as a PH regulator, formaldehyde (37%) 25.3 ml as reducer. Make an above be a 240 ml solution. It adjusted to PH 12.8.

The whole quantity of this solution is thrown into the slurry of an above-mentioned platinum-carbon catalyst at once.

1 minute was dispersed with the ultrasonic homogenizer, stirring.

And this is filtered after stirring a 1 hour. Furthermore several times washing was carried out with water until cleaning liquid became neutral.

Finally, it heated before and after 900 degree C under the hydrogen air current, and the alloying process of the platinum particle and copper in the catalyst was carried out.

[0010]

The phosphoric acid type fuel battery platinum alloy catalyst of the each Example produced as mentioned above, Base metal independent particles, such as a platinum independent particle, nickel, cobalt, iron, and copper, are

金属単独粒子が極めて少なく、また白金と卑金属との合金組成比が1:1に近づき、触媒中の合金微粒子間の組成比の偏りが著しく減少した。そしてこれら白金合金触媒をりん酸型燃料電池に用いた処、耐溶出性が著しく向上し、半電池での初期活性が2~5%向上した。尚、カーボン担体上の白金は、無電解めっきのアクティベーターとなり、白金上には必ずめっき成分が析出する。従って、一般に無電解めっきのアクティベーターとして知られるパラジウムでも同様にめっき成分が析出するので、パラジウムやそれらの混合物や合金でも同様に耐溶着性、活性に優れた触媒を得ることが可能であることを付言しておく。

[0011]

【発明の効果】

以上の通り本発明のりん酸型燃料電池用白金合金触媒の製造方法によれば、白金単独粒子や卑金属単独粒子が極めて少なく、また白金と卑金属との合金組成比の偏りが著しく少なく、りん酸型燃料電池に用いた際の耐溶出性及び活性を向上できる白金合金触媒を得ることができる。

very few. Moreover the alloy composition ratio of platinum and base metal approaches 1:1. Deviation of the composition ratio between the alloy microparticles in the catalyst reduced remarkably.

And when these platinum alloy catalyst was used for the phosphoric acid type fuel cell, dissolubility-resistant improved remarkably and the initial stage activity in a halfcell improved 2-5%.

In addition, the platinum on a carbon carrier makes the activator of an electroless plating.

Definitely on platinum, a plating component precipitates.

Therefore, since a plating component precipitates similarly palladium generally known as an activator of an electroless plating, it adds that it is possible to obtain a catalyst which was excellent in welding-resistant property and the activity similarly with palladium, their mixtures, and the alloy.

[0011]

[EFFECT OF THE INVENTION]

As mentioned above according to the manufacturing method of the phosphoric acid type fuel battery platinum alloy catalyst of this invention, a platinum independent particle and a base metal independent particle are very few. Moreover deviation of the alloy composition ratio of platinum and base metal is remarkably few. The platinum alloy catalyst which can improve the dissolubility-resistant and the activity at the time of using for a phosphoric acid type fuel cell can be obtained.



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MANUFACTURING METHOD OF PLATINUM
ALLOY CATALYST FOR PHOSPHORIC ACID TYPE
FUEL CELL

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Abstract

(57)【要約】

【目的】

触媒中の白金又は白金合金の粒子上に卑金属を担持し合金化して、白金単独粒子や卑金属単独粒子を少なくし、且つ合金組成比の偏りをより小さくして、りん酸型燃料電池に用いた際の耐溶出性及び活性を向上させることのできるりん酸型燃料電池用白金合金触媒を作ることのできる方法を提供する。

【構成】

白金又は白金合金をカーボン粉末に担持した触媒を温水に浸し攪拌しながら超音波ホモジナイザーで分散し、然る後この分散した触媒に、クロム、マンガ、鉄、コバルト、ニッケル、銅の1種又は2種を無電解めっきし、触媒中の白金又は白金合金粒子と合金化することと特徴とするりん酸型燃料電池用白金合金触媒の製造方法。

(57) [Abstract]

[Objective]

Bearing base metal in platinum in catalyst, or on particle of the platinum alloy alloying doing, it decreases platinum alone particle and base metal alone particle, at the same time makes deviation of alloy composition ratio smaller, case where it uses for phosphoric acid type fuel cell elution resistance and activity it offers method which can make platinum alloy catalyst for phosphoric acid type fuel cell which can improve.

[Constitution]

While soaking catalyst which bears platinum or platinum alloy in the carbon powder in warm water and agitating manufacturing method, of platinum alloy catalyst for the phosphoric acid type fuel cell where it disperses with ultrasonic homogenizer, after that this in catalyst which is dispersed, electroless plating it does 1 kind or 2 kinds of chromium, manganese, iron, cobalt, nickel, copper, platinum or platinum alloy particle and alloying in catalyst does and makes feature

Claims

【特許請求の範囲】

【請求項 1】

[Claim(s)]

[Claim 1]

白金又は白金合金をカーボン粉末に担持した触媒を温水に浸し攪拌しながら超音波ホモジナイザーで分散し、然る後この分散した触媒に、クロム、マンガン、鉄、コバルト、ニッケル、銅の 1 種又は 2 種を無電解めっきし、触媒中の白金又は白金合金粒子と合金化することを特徴とするりん酸型燃料電池用白金合金触媒の製造方法。

Specification

【発明の詳細な説明】

【0001】

【産業上の利用分野】

本発明は、りん酸型燃料電池用白金合金触媒の製造方法に関する。

【0002】

【従来の技術】

従来、りん酸型燃料電池用白金合金触媒を製造するには、白金をカーボン粉末に担持した触媒を水に濡らし、これに合金成分となる 1 種又は 2 種の卑金属を含む溶液、即ちクロム、マンガン、鉄などは硝酸塩溶液、コバルト、ニッケル、銅などはアンモニア性アルカリ性溶液として加えて混合し、1 時間程度攪拌してスラリー状にした後、乾固させた。

その後水素気流下で 900 deg C 前後に加熱して、還元、合金化処理を行っていた。

この従来の製造方法で製造できる白金合金触媒は、合金組成比がモル比で Pt:卑金属=1:1 が目標であるにもかかわらず、卑金属を含む溶液の混合量を増やしても、また長時間攪拌しても 1:0.3 程度までしか合金化されない。

また白金を担持させたカーボン粉末の触媒を溶液と混合させた後乾固させる為、卑金属成分が塩の結晶となって不均一に析出し、触媒中で卑金属成分の偏在が起こる。

これを水素中で合金化処理を行っても卑金属と合金となった白金合金のほぼ白金単独或いは卑金属単独の粒子でもでき、特に卑金属単独の粒子は酸で容易に洗い流されてしまう。

【0003】

【発明が解決しようとする課題】

そこで本発明は、触媒中の白金又は白金合金

While soaking catalyst which bears platinum or platinum alloy in the carbon powder in warm water and agitating manufacturing method. of platinum alloy catalyst for the phosphoric acid type fuel cell where it disperses with ultrasonic homogenizer, after that this in catalyst which is dispersed, electroless plating it does 1 kind or 2 kinds of chromium, manganese, iron, cobalt, nickel, copper, platinum or platinum alloy particle and alloying in catalyst does and makes feature

【Description of the Invention】

【0001】

【Field of Industrial Application】

this invention regards manufacturing method of platinum alloy catalyst for phosphoric acid type fuel cell.

【0002】

【Prior Art】

Until recently, platinum alloy catalyst for phosphoric acid type fuel cell is produced, it soaked the catalyst which bears platinum in carbon powder in water, it mixed ammonia alkaline solution as for solution, namely as for chromium, manganese, iron etc nitrate salt solution, cobalt, nickel, copper etc which include base metal of 1 kind or 2 kinds which becomes alloy component in this adding, 1 hour extent agitated and after making slurry, dry solid it did.

After that heating to approximately 900 deg C under hydrogen stream, it reduced and it treated alloying.

platinum alloy catalyst which can be produced with this conventional manufacturing method, alloy composition ratio being the mole ratio, Pt: base metal=1:1 it is a goal of increasing mixed amount of solution which includes base metal in spite, even when, in addition lengthy agitating, 1: alloying is done to only 0.3 extent.

In addition in order after solution and mixture dry solid to do the catalyst of carbon powder which bears platinum, base metal component becoming crystal of salt, it precipitates to nonuniform, maldistribution of the base metal component happens in catalyst.

This treating alloying in hydrogen, also other platinum alone of platinum alloy which becomes base metal and alloy or particle of base metal alone is possible, particle of especially base metal alone is washed away easily with acid.

【0003】

【Problems to be Solved by the Invention】

Then this invention, bearing base metal in platinum in catalyst

の粒子上に卑金属を担持し合金化して、白金単独粒子や卑金属単独粒子を少なくし、且つ合金組成比を現状の 1:0.3 から 1:1 に近づけて触媒中の合金微粒子間の合金組成比の偏りをより小さくして耐溶出性及び活性を向上させることのできるりん酸燃料電池用白金合金触媒の製造方法を提供しようとするものである。

[0004]

【課題を解決するための手段】

上記課題を解決するための本発明のりん酸型燃料電池用白金合金触媒の製造方法は、白金又は白金合金をカーボン粉末に担持した触媒を温水に浸し攪拌しながら超音波ホモジナイザーで分散し、然る後この分散した触媒に、クロム、マンガン、鉄、コバルト、ニッケル、銅の 1 種又は 2 種を無電解めっきし、触媒中の白金又は白金合金粒子と合金化すること特徴とするものである。

[0005]

【作用】

上記のように本発明のりん酸型燃料電池用白金合金触媒の製造方法では、白金又は白金合金をカーボン粉末に担持した触媒を分散し、これにクロム、マンガン、鉄、コバルト、ニッケル、銅の 1 種又は 2 種を無電解めっきし、触媒中の白金又は白金合金粒子と合金化するので白金単独粒子や卑金属単独粒子が少なくなり、且つ合金組成比の偏りが著しく減少し、触媒の耐溶出性及び活性が向上する。

[0006]

【実施例】

本発明のりん酸型燃料電池用白金合金触媒の製造方法の実施例を説明する。

[0007]

(1) 白金を 2.85g 含む白金-カーボン触媒 12.85g を沸とう水 180ml に浸し、攪拌しながら超音波ホモジナイザーで分散させた。

次に塩化ニッケル 1.94g、塩化コバルト 1.93g、錯化剤として酒石酸ナトリウム 29.58g、還元剤として塩酸ヒドラジン 13.49g を 320ml の水溶液とし、50%NaOH 溶液で pH を 12.8 に調整した溶液を、前記白金-カーボン触媒のスラリーに全量一度に投入し、攪拌しながら超音波ホモジナイ

and or on particle of platinum alloy alloying doing, to decrease platinum alone particle and the base metal alone particle, at same time alloy composition ratio present state 1:0.3 Bringing close to to 1:1, making deviation of alloy composition ratio between alloy microparticle in catalyst smaller, elution resistance and activity it is something which it tries to offer manufacturing method of platinum alloy catalyst for phosphoric acid fuel cell which can improve.

[0004]

【Means to Solve the Problems】

While manufacturing method of platinum alloy catalyst for phosphoric acid type fuel cell of this invention in order to solve above-mentioned problem, soaking catalyst which bears the platinum or platinum alloy in carbon powder in warm water and agitating it disperses with ultrasonic homogenizer, after that this in catalyst which is dispersed, electroless plating it does 1 kind or 2 kinds of chromium, manganese, iron, cobalt, nickel, copper, It is something which platinum or platinum alloy particle and alloying in the catalyst it does and makes feature.

[0005]

【Working Principle】

As description above with manufacturing method of platinum alloy catalyst for phosphoric acid type fuel cell of the this invention, to disperse catalyst which bears platinum or platinum alloy in the carbon powder, electroless plating to do 1 kind or 2 kinds of chromium, manganese, iron, cobalt, nickel, copper in this, because platinum or platinum alloy particle and alloying in catalyst it does, platinum alone particle and base metal alone particle decrease, at same time deviation of alloy composition ratio decreases considerably, elution resistance and activity of catalyst improve.

[0006]

【Working Example(s)】

Working Example of manufacturing method of platinum alloy catalyst for phosphoric acid type fuel cell of this invention is explained.

[0007]

While soaking platinum-carbon catalyst 12.85g which (1) platinum 2.85 g is included in boiling water reactor 180 ml, agitating it dispersed with the ultrasonic homogenizer.

While next designating hydrazine hydrochloride 13.49g as aqueous solution of 320 ml as the sodium tartrate 29.58g, reductant as nickel chloride 1.94g, cobalt chloride 1.93g, complexing agent, throwing solution which adjusted pH 12.8 with 50% NaOH solution, at total amount one time in slurry of aforementioned platinum-carbon catalyst, agitating 2

Pl Ni Co

ザーで 2 分間分散させた。

そして 1 時間程攪拌した後、これを濾過し、さらに洗浄液が中性になるまで水で数回洗浄した。

最後に水素気流下で 900 deg C 前後に加熱して触媒中の白金粒子とニッケル及びコバルトを合金化処理した。

[0008]

(2)白金を 1.95g 含む白金-カーボン触媒 8.8g を沸とう水 120ml に浸し、攪拌しながら超音波ホモジナイザーで分散させた。

次に硝酸ニッケル 1.45g、硝酸鉄 2.05g 錯化剤として酒石酸ナトリウム 18.42g 還元剤として、塩酸ヒドラジン 31.24g を 200ml の溶液とし、50%NaOH 溶液で pH を 12.8 に調整した溶液を、前記白金-カーボン触媒のスラリーに全量一度に投入し、攪拌しながら超音波ホモジナイザーで 1 分間分散させた。

そして 1 時間程攪拌した後、これを濾過し、さらに洗浄液が中性になるまで水で数回洗浄した。

最後に水素気流下で 900 deg C 前後に加熱して触媒中の白金粒子とニッケル及び鉄を合金化処理した。

[0009]

(3)白金を 2.85g 含む白金-カーボン触媒 12.85g を沸とう水 180ml に浸し、攪拌しながら超音波ホモジナイザーで分散させた。

次に硫酸銅 3.53g、錯化剤として酒石酸塩 7.59g、PH 調整剤として水酸化ナトリウム 5.06g、還元剤としてホルムアルデヒド (37%)25.3ml を 240ml の溶液とし PH12.8 に調整した。

この溶液を前記白金-カーボン触媒のスラリーに全量一度に投入し、攪拌しながら超音波ホモジナイザーで 1 分間分散させた。

そして 1 時間程攪拌した後、これを濾過し、さらに洗浄液が中性になるまで水で数回洗浄した。

最後に水素気流下で 900 deg C 前後に加熱して触媒中の白金粒子と銅を合金化処理した。

[0010]

上記のように製造した各実施例のりん酸型燃料電池用白金合金触媒は、白金単独粒子やニッ

min it dispersed with ultrasonic homogenizer.

Until and about 1 hour after agitating, this is filtered, furthermore wash liquid becomes neutral, several times you washed with water.

Heating to approximately 900 deg C lastly under hydrogen stream, alloying it treated platinum particle and nickel and cobalt in catalyst.

[0008]

While soaking platinum-carbon catalyst 8.8g which (2) platinum 1.95 g is included inboiling water reactor 120 ml, agitating it dispersed with the ultrasonic homogenizer.

While next designating hydrazine hydrochloride 31.24g as solution of 200 ml as the sodium tartrate 18.42g reductant as nickel nitrate 1.45g, iron nitrate 2.05g complexing agent, throwing solution which adjusted pH 12.8 with 50% NaOH solution, at total amount one time in slurry of aforementioned platinum-carbon catalyst, agitating 1 minute it dispersed with ultrasonic homogenizer.

Until and about 1 hour after agitating, this is filtered, furthermore wash liquid becomes neutral, several times you washed with water.

Heating to approximately 900 deg C lastly under hydrogen stream, alloying it treated platinum particle and nickel and iron in catalyst.

[0009]

While soaking platinum-carbon catalyst 12.85g which (3) platinum 2.85 g is included inboiling water reactor 180 ml, agitating it dispersed with the ultrasonic homogenizer.

Next as copper sulfate 3.53g, complexing agent formaldehyde (37%) it designated 25.3 ml as solution of 240 ml as sodium hydroxide 5.06g, reductant as tartrate 7.59g, pH adjustment medicine and adjusted the pH 12.8.

While throwing this solution at total amount one time in slurry of the aforementioned platinum-carbon catalyst, agitating 1 minute it dispersed with ultrasonic homogenizer.

Until and about 1 hour after agitating, this is filtered, furthermore wash liquid becomes neutral, several times you washed with water.

Heating to approximately 900 deg C lastly under hydrogen stream, alloying it treated platinum particle and copper in catalyst.

[0010]

As description above platinum alloy catalyst for phosphoric acid type fuel cell of each Working Example which

ケル、コバルト、鉄、銅などの卑金属単独粒子が極めて少なく、また白金と卑金属との合金組成比が1:1に近づき、触媒中の合金微粒子間の組成比の偏りが著しく減少した。

そしてこれら白金合金触媒をりん酸型燃料電池に用いた処、耐溶出性が著しく向上し、半電池での初期活性が2-5%向上した。

尚、カーボン担体上の白金は、無電解めっきのアクティベーターとなり、白金上には必ずめっき成分が析出する。

従って、一般に無電解めっきのアクティベーターとして知られるパラジウムでも同様にめっき成分が析出するので、パラジウムやそれらの混合物や合金でも同様に耐溶着性、活性に優れた触媒を得ることが可能であることを付言しておく。

【0011】

【発明の効果】

以上の通り本発明のりん酸型燃料電池用白金合金触媒の製造方法によれば、白金単独粒子や卑金属単独粒子が極めて少なく、また白金と卑金属との合金組成比の偏りが著しく少なく、りん酸型燃料電池に用いた際の耐溶出性及び活性を向上できる白金合金触媒を得ることができる。

is produced, platinum alone particle and nickel, cobalt, iron, copper or other base metal alone particle quite were little, in addition the alloy composition ratio of platinum and base metal 1: got near to 1, deviation of the composition ratio between alloy microparticle in catalyst decreased considerably.

And place where these platinum alloy catalyst are used for phosphoric acid type fuel cell, elution resistance improved considerably, initial activity with half battery improved 2 - 5%.

Furthermore platinum on carbon support, it becomes activator of electroless plating, plating component precipitates by all means on platinum.

Therefore, generally because plating component precipitates in same way even with palladium which is known as activator of electroless plating, the catalyst which even in palladium and mixture of those and alloy is superior in same way in seizure resistance, activity is obtained, it is possible, you say in addition.

【0011】

【Effects of the Invention】

Sort above according to manufacturing method of platinum alloy catalyst for phosphoric acid type fuel cell of the this invention, platinum alone particle and base metal alone particle quite are little, in addition deviation of alloy composition ratio of platinum and base metal is little considerably, the case where it uses for phosphoric acid type fuel cell elution resistance and activity platinum alloy catalyst which it can improve can be acquired.